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Description.

The invention relates to a process for thermal polymerization, the polycondensation or the condensation of monomeric synthetic matters, like the vinyl monomers or of the synthetic with molecular weight relatively low but setting matters, like urethans, of the unsaturated resins polyester, compounds allyl, resins containing phenol formaldehyde and similar, in porous materials, like in particular wood, concrete-foam and similar.

Conformément <RTI ID=1.1> å< /RTI> the invention, it is expected that the controlled adduction of heat, for adjustment of the temperature of starting of exothermic chemical reactions or the continuation of endothermic matter reactions syn <RTI ID=1.2> thetic< /RTI> monomers or liquids as well as the elimination of surplus heat during exothermic chemical reactions take place by means of thermal media of transfer present in the liquid state in the range of the temperatures of the chemical reactions which proceed, for example for polymerization in-situ of monomeric methyl methacrylate in wood, it moreover is envisaged to use like thermal liquid of support of the matters not reacting chemically with the synthetic matters present in porous material, to remove after polymerization the thermal media of transfer of surfaces of these materials using a suitable solvent and to separate if necessary from the solution obtained the substances having been useful has the impregnation.

The new process is distinguished from the polymerization of monomers in-situ in wood by the fact that <RTI ID=2.1> one< /RTI> uses instead of air and of gases which are bad conductive of heat, like thermal medium of support, of the inert liquids with high thermal conductibility, coming into direct contact with material to polymerize, while making there bathe this last systematically and with a controlled agitation, guaranteeing of this fact a adduction and an exactly controlled elimination of heat, appreciably more important, distributed on all the surface of material, limiting the oxygen admission during polymerization, decreasing the losses in monomers at the time of polymerization and increasing the speed of the course of the reaction.

By German request DOS N02 040.356, one also was informed of a version of the process of hardening per ionizing radiation in which, after <RTI ID=2.2> impregnated it< /RTI> tion of a porous object with a polymerizable liquid, this object is surrounded by a liquid layer forming a protective body. This layer is solidified before RTI <ID=2 does not start.3> the aperture< /RTI> ration of irradiation leading to polymerization and, even if the irradiation leads to a new liquefaction partial of the protective body, the matter of this protective body cannot be used for the control of the adduction and the elimination of heat, since its temperature is fixed unambiguous possible by the geometrical configuration and the amount of radiation used.This protective body thus serves only <RTI ID=2.4> A< /RTI> to protect the monomer from the access of the air.

The known methods of the exothermic monomeric synthetic matter polymerization in porous materials have the disadvantage that for the course of the manufacturing process it is necessary to at least twice modify the arrangement of the products, i.e. the latter will be individually to handle in order to avoid accumulations of heat at the time of polymerization. This <RTI ID=2.5> /RTI< process> is expensive, just as the known equipment of manufacture are appreciably more expensive than those to use for the new process.

<RTI ID=3.1> I1< /RTI> is indeed known to use for example polyethyleneglycol like thermal support in small aggregates of vulcanization to electric heating and for baths of immersion for vulcanization without pressure of solid articles out of rubber. News, is however the use of media of thermal support liquid, such as for example of polyethyleneglycol for polymerization in-situ

of monomers, for example of liquid methyl methacrylate in impregnated wood or the use of porous synthetic matter materials impregnated liquidate, as well as the resolution of the problems involved in this spot.

In accordance with the invention, the parts can in the first versed or piled up time being, in disorder or in an ordered way, in a perforated basket, without another handling of the individual parts and to thus traverse all the operating cycle, begin with swelling, drying, evacuation, impregnation, controlled polymerization, washing, and finishing with hardening and air-conditioning.

The critical problems of distribution of heat at the time of the polymerization of materials according to known processes' are removed by the method in conformity with the invention.

The adduction and the elimination of heat become independent of the arrangement of the parts in <RTI ID=3.2> polymerisator.</RTI>

The new process of polymerization in-situ of the wood proposed like medium of adduction and elimination of the heat of the inert liquids, like polyethyleneglycol, glycerin, of melted waxes, pyridine, of chlorinated hydrocarbons, naphthalene, chlorinated naphthalene, metal alloys at low melting point <RTI ID=3.3> (500C),< /RTI> of <RTI ID=3.4> paraffinelastéarine,< /RTI> of oils, and matters similar, not forming a direct compound with the monomers or the impregnated wood of a students'rag procession Re or of a synthetic matter and only <RTI ID=4.1> one< /RTI> can again remove by washing of the surface of wood <RTI ID=4.2> polymerizes.</RTI>

Wood or the part impregnated with the catalysed liquid monomer, for example with methyl methacrylate <RTI ID=4.3> (4M)< /RTI> being in disorder or piled up in a perforated basket, are plunged in the liquid of thermal support inert and left in this one, in the absence of oxygen in air and under the pressure provided by the level of the liquid, the temperature being controlled and <RTI ID=4.4> reglablte,< /RTI> so that it bathes entirely in the thermal support whose agitation is controlled, until the product reaches the temperatures of starting of polymerization and which the exothermic reaction and the hardening of the synthetic matter in wood can be completed at exactly definite and controllable temperatures.

During this operation, a detailed attention is allotted to the fact that until the end of exothermic polymerization the temperature, for example for wood, inside the part does not go up above <RTI ID=4.5> 90-95 C,< /RTI> to avoid a degasification and an exudation of monomer or still liquid synthetic matter or formation of vapors.

The heat of reaction to be brought to the surface of the part or to eliminate from this one is regulated on this occasion by a passage controlled through the container of polymerization and the adjustment of the temperature (cooling).

At the end of the chemical reaction and after adjustment of tem <RTI ID=4.6> pérature< /RTI> of hardening (for example of 1050C approximately), the perforated basket filled with polymerized wood is withdrawn and subjected to an operation of washing, to remove the liquid of thermal support retained on the surface of wood or basket (approximately 2 5% of the weight of wood).

Figures 1 and 2 show for example the execution of the process of polymerization and washing, as it was carried out on a laboratory scale.

The container of polymerization P, for example, is filled with polyethyleneglycol at a temperature of <RTI ID=5.1> 60-70 " C.</RTI> This liquid of thermal support is maintained at

the temperatures wished using an exchanger of heat 2 and a circulating pump 1. The basket perforated 3 filled with impregnated wood of catalysed the methyl methacrylate monomer is then immersed in the thermal liquid of support.

<RTI ID=5.2> /RTI< By-continuation> of the regular passage of the liquid through the perforated basket, each piece of wood is heated in a uniform way and the exothermic heat of formed reaction is eliminated in proportions <RTI ID=5.3> desired< /RTI> polymerization take place, by using methyl methacrylate (MAM), for example in <RTI ID=5.4> one untied< /RTI> of 30-45 minutes, the consecutive hardening of the synthetic matter in wood within 10-15 minutes, for a temperature of 1050C.

The perforated basket filled of finished polymerized wood then left the container of polymerization, disencumbered on surfaces of the surplus of the matter being used as thermal support by means of an apparatus vibrating, and plunged, at preset temperatures given, from example <RTI ID=5.5> 60-90 C,< /RTI> during 3 minutes in <RTI ID=5.6> /RTI< a-container> of washing I, filled of a solution, for example at 20%, of polyethyleneglycol (PEG) with 800C for example. For each load of 100 kg polymerized wood, approximately 3-6 kg of PEG passes in the 150 1 of the liquid of washing whose concentration in PEG passes then to approximately 23%.

Washing takes place under turbulent flow of the liquid of washing.

The perforated basket containing wood polymerized <RTI ID=5.7> prélavé< /RTI> is now transferred, according to Figure 1, of the container of washing I in the container of washing <RTI ID=5.8> II,< /RTI> or 100 kg of wood Po <RTI ID=5.9> lymerized< /RTI> make enter approximately 2-3 kg of liquid to 23 <RTI ID=5.10> %< /RTI> of PEG, therefore 0,7 kg of PEG in 150 <RTI ID=5.11> 1< /RTI> of liquid of washing It with 800C (0,45% of PEG).

In container III final washing using hot water takes place. Like, the 150 1 of hot water in container III enters only 2 1 of the liquid which was retained on surfaces, containing 9 G of PEG, it does not remain, after washing in container III, on the surface of 100 kg polymerized wood that 3 1 of liquid, containing 8 G of PEG. After the exit of the polymerized wood of container III for drying of surface, the surface of polymerized wood is then almost free from <RTI ID=6.1> EP & </RTI>

After completion of the process of polymerization one restores in the container of polymerization P the same level of thermal support, by bringing container A for example 5 kg of PEG by 100 kg of polymerized wood, since with each load of wood approximately 5 1 of PEG is transported in the container of washing I. One can then introduce a new load to be polymerized.

At the end of the process of washing one introduces for each time 100 kg of wood polymerized for example 25 kg of liquid PEG of the container of washing I into the storage tank of the PEG B and it runs out of the container of washing <RTI ID=6.2> II< /RTI> 20 1 of liquid of washing towards container I, 20 1 of liquid of washing of container III towards container <RTI ID=6.3> II< /RTI> and 20 1 of hot water of the storage tank of hot water V towards container III.

By that, the levels of the liquids in the containers A, I, It and III are given in their initial state and the next load of washing can start. This process can be carried out under automatic control.

Since it is necessary, by container of polymerization and load from wood, 50 to 75 minutes for the polymerization and final hardening and for the operation of washing in the 3 containers only of 12 A approximately 15 minutes, one can set up for each time a cleaning facility (I, <RTI ID=6.4> It,< /RTI> III) approximately 4-5 containers of polymerization P. When the containers

of polymerization have a capacity of each time 400-500 kg of polymerized wood, one can make pass, in continuous exploitation, per hour of operation, 5 loads of a total of 2 tons or approximately 2 m3 of polymerized wood.

Arrangement prescribes of 4-5 containers of polymerization and of 3 containers of washing can also be replaced by the combination of a container of polymerization with a container of washing W and the addition of 4-6 storage tanks of PEG and water of washing to various concentrations, or the operation of washing takes place by transvasing by a pump the solutions of washing of a storage tank via the container of washing W in the next storage tank, in accordance with Figure 2.

The capacity of flow of the installation of polymerization and washing described above is in theory of approximately 48 tons of wood polymerized of 24 hours.

According to wood samples' of which one lays out until now, the specific characteristics of wood are equivalent <RTI ID=7.1> A< /RTI> those of the products obtained using other methods of polymerization.

As liquids of washing for polymerized materials one will be useful oneself of water when one used polyethyleneglycol or media of thermal support water soluble.

When stearin is used, paraffin, waxes, hydrocarbons <RTI ID=7.2> chloresdunaphtalene< /RTI> etclike thermal support, one will make use of organic inert solvents, the aromatic series aliphatic- or most suitable and the least expensive, not reacting preferably with the synthetic matter contained in porous material or with surfaces of this material and which at the same time are not a solvent for the synthetic matter polymerized in material. One can for example to this end use chlorinated hydrocarbons, similar benzene and his derivatives and other usual solvents.

The solutions of washing, enriched during the closed loop according to Figures' 1 and 2, are then distilled and the substances of exchange <RTI ID=8.1> /RTI< thermics> recovered; solvents being re-used in the process.

During the polymerization of the synthetic matters in material, from small quantities of monomers or slightly polymerized synthetic matters pass in the thermal liquid of support. An occasional regeneration or purification of the thermal liquid of support will be thus necessary.

In the event of a methyl methacrylate polymerization in wood, not controlled or too rapid, of the resins of still liquid polymethylmethacrylate can for example exude pores of wood.

The substances which separate float then on the surface of the thermal liquid of support and can be removed using a separator for matters surnageantes.

Small quantities of monomers, by wood load, can also penetrate in the heat exchanger liquid and be polymerized within this one. By using polyethyleneglycol as heat exchanger liquid this one should be regenerated after each time 10-20 polymerized wood loads.

The separation of the polymethylmethacrylate in the PEG is obtained advantageously by flocculation, by diluting the PEG with water. In the example of execution represented, flocculation takes place by adding 50 1 of hot water to 900 kg of PEG after 13-14 loads in the aggregate of purification D.

In a solution containing from 25 to 35% of PEG, the polymethylmethacrylate <RTI ID=8.2> (Poly-iM)< /RTI> are flocculated with fine grain and can be filtered. The solution of filtered PEG can be used for the pre-swelling of wood in the cyclic process for dimensional stabilization

of wood and dried Poly-MAM is dissolved in <RTI ID=9.1> MAM< /RTI> and added to the solution of MAM intended for the impregnation.

Since <RTI ID=9.2> one< /RTI> uses for the manufacture of 100 kg wood polymerized approximately 15% of PEG for dimensional stabilization, it is advantageous to withdraw, after each polymerization of a wood load, by 100 kg of polymerized wood, approximately 15 kg of heat exchanger liquid containing the PEG, of the tank of the polymerisator and to replace them by 15 kg of fresh PEG. One thus avoids an undesirable enrichment of the PEG in the tank of the polymerisator, so that <RTI ID=9.3> one< /RTI> can work without raw material loss in a direct cyclic process, with insertion of a filter to retain the flocculated synthetic matter.

CLAIMS

1. Process for thermal polymerization, polycondensation or the condensation of monomeric synthetic matters, like the vinyl monomers or the low-weight molecular but setting matters synthetic, like urethans, the resins polyester not <RTI ID=10.2> saturéeslescomposés< /RTI> <RTI ID=10.3> allyl, 1esré-< /RTI> sines containing formaldehyde of phenol and similar in porous materials, like in particular wood, the concrete-foam and similar, characterized in that the controlled adduction of heat, for adjustment of the temperature of starting of the exothermic chemical reactions or the continuation of endothermic reactions applying to monomeric synthetic matters or liquids and the elimination of surplus heat during exothermic chemical reactions, has place by means of media of thermal transfer present in the liquid state in the range of temperatures of the chemical reactions which proceed for example for polymerization in-situ of monomeric methyl methacrylate in wood, and in what <RTI ID=10.4> one< /RTI> uses as thermal liquid of support of the matters not reacting chemically with the matters synthéen this ticks present in material <RTI ID=10.5> porous, Xque< /RTI> <RTI ID=10.6> one< /RTI> removes moreover after polymerization the thermal media of transfer of surfaces of these materials using a solvent <RTI ID=10.7> aDDronrié< Cl> /RTI <RTI ID=10.8> et' that 'one< /RTI> separates if necessary this solution from the substances having been used for the impregnation.

2. Process according to claim 1, characterized in that materials to be subjected to the chemical reaction, impregnated of <RTI ID=10.9> matters svnthétiaues.</RTI> are immercrés in a liquid of trans <RTI ID=10.10> in this ---------</RTI> <RTI ID=10.11> tert< /RTI> thermics <RTI ID=10.12> etlque< /RTI> <RTI ID=10.13> one< /RTI> regulates, in order to obtain a adduction and a controlled elimination of heat, the temperature and the agitation of the thermal support in which will have to bathe material, by suitable measurements like are the utili sation <RTI ID=11.1> of échangeurg< adjustable> /RTI of heat and installations of circulation of also adjustable liquids.

3. Process according to one of claims 1 to 2, characterized in that <RTI ID=11.2> one< /RTI> uses like <RTI ID=11.3> liquids< thermal> /RTI support <RTI ID=11.4> (</RTI> it of polyethyleneglycol, <RTI ID=11.5> stearin, Jparaffine,< /RTI> of waxes, of heavy oils, pyridine, of chlorinated hydrocarbons, chlorinated naphthalene, chlorinated diphenyls or alloy of Wood.

4. Proceeded according to one of claims 1 to 3, characterized in that, for the elimination of the liquid of thermal support retained on the surface of materials, one makes follow, when the chemical reaction in material is finished, an operation of washing with water for

polyethyleneglycol, or with halogenous or aromatic hydrocarbons for paraffins, similar waxes and matters.

5. Process according to one of claims 1 to 4, characterized in that <RTI ID=11.6> one< /RTI> uses as thermal liquid of support, for example for polymerization in-situ of the polyethyleneglycol 1000 - 1500, which is then, after enrichment with counter-current in closed loop, brought during an operation of washing including/understanding from 2 to 4 levels, with a content of 20 polyethyleneglycol 30% of the liquid of washing of the first level.

6. Process according to one of claims 1 to 5, characterized in that, for the polymerization of vinyl monomers in wood, one orders by cooling and elimination of the heat of reaction the temperature of the liquid of thermal support and the regular entourage, adjustable of the parts by the bath during the exothermic reaction, in such way that the heat of polymerization created inside the parts cannot exceed 85-950C until the end of the reaction of hardening.

7. Proceeded according to one of claims 1 to 6, characterized in that one flocculates and filters the synthetic matters last in the exchanging liquid of heat containing of polyethyleneglycol during the polymerization of the monomers in it by dilution with water <RTI ID=12.1> et/ue< /RTI> <RTI ID=12.2> one< /RTI> adds the synthetic matter particles filtered and dried to the solution of the monomer intended for the impregnation.

8. Installation for the execution of the process according to one of claims 1 to 7, characterized in that it is composed of a container chauffable for the liquid of thermal transfer (A), of a container of polymerization (P), comprising devices to maintain constant and regulate the temperature of the liquid of thermal support in a range of <RTI ID=12.3> 20-16O0C< /RTI> as well as a device of circulation, an exchanger of heat and a device of temperature control for the thermal medium of support, of a container to receive the thermal medium of used support and the liquid of washing, of a device (D) of filtering, regeneration and possible concentration of the liquid of washing and exchanging liquid of heat and comprises moreover containers of washing (I), (II) and (III), of which <RTI ID=12.4> one< /RTI> at least comprises devices of circulation and heat transfer to regulate the temperature of the liquid of washing and an additional container (C) for liquid of pure washing as well as other tanks for the liquid of washing.

9. Installation according to claim 8, characterized in that it is provided a lifting gear with the help of which a basket of load <RTI ID=12.5> (IV),< /RTI> filled of impregnated porous material, can be introduced successively into the container of polymerization (P) then (after polymerization of materials) initially last through the container of washing (I), then by the container of washing (II) and the container of washing (III) to go then, after drying and air-conditioning of the polymerized product, to manufacture.

10. Installation according to one of claims 8 and 9, carac terized in what several containers of polymerization (P) are coupled by valves mechanically operated automatically with only one container of washing (I) and with 3-6 water tanks and a pump, in such way that basket <RTI ID=13.1> D< /RTI> charges (IV) is brought only only once container of polyméri <RTI ID=13.2> sation (p) in the container of washing (I) and in what /RTI< washing> has place by successive filling and emptying and transfer by the pump of the solution of washing, starting from the storage tanks.

11. Installation according to claims' 8 to 10, characterized in that the container of polymerization (P) is equipped with a separator for the solid polymer particles, supplies to survive by gas bubbles.